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Calorimetric investigation of precipitation from solid solutions of N in α-Fe

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With 3 figures in the text

1. Summary. Specimens of pure iron charged with nitrogen have been heated at various constant temperatures between 170 and 575 °C to obtain the equilibrium states between nitrogen dissolved in α-iron and the nitride Fe_4N. After quenching, the precipitation of nitrogen from the solution has been studied at constant temperatures of 70 or 94 °C by measuring the power of the evolution of heat as a function of time. Integration of the power-time curves thus obtained gives the total emission of heat during the precipitation process. From this heat and its dependence on temperature, thermodynamic calculations give the heat of solution and the solubilities of nitrogen at various temperatures.

2. Experimental arrangements. The calorimetric method used for the present measurements is in principle the same as that used earlier in this laboratory for the study of various transformations in alloys. The specimen is kept in a vessel with very constant temperature, and a series of thermocouples connected to a sensitive galvanometer are arranged between the specimen and the walls of the vessel in such a way, that the deflection of the galvanometer is proportional to the excess of temperature of the specimen caused by the evolution of heat due to the transformation. To obtain quantitative results the apparatus is calibrated with a known amount of Peltier heat evolved by a current through a thermocouple put into a boring in the specimen.

The central part of the present apparatus is shown in Fig. 1. The specimen is a cylinder with a height of 50 mm and a diameter of 18 mm. It has a central boring, in which is placed the junction of a Pt-PtRh-couple used both to produce the Peltier heat during the calibration and for the measurement of the temperature during the initial heat treatment of the specimen. There are also eight other borings in order to shorten the way of diffusion during the preparatory decarburization and nitration processes. The specimen is introduced from above in a vertical glass tube. Between this tube and the cylindrical wall of a thermostat, there is a hollow cylindrical tube of isolite with 30 couples of copper-constantan wound in series in such a way that odd junctions are at the inner and even at the outer side of the tube.

The thermostat was a water-vapour thermostat, and as the effects to be measured were very small, special precautions were necessary in order to keep

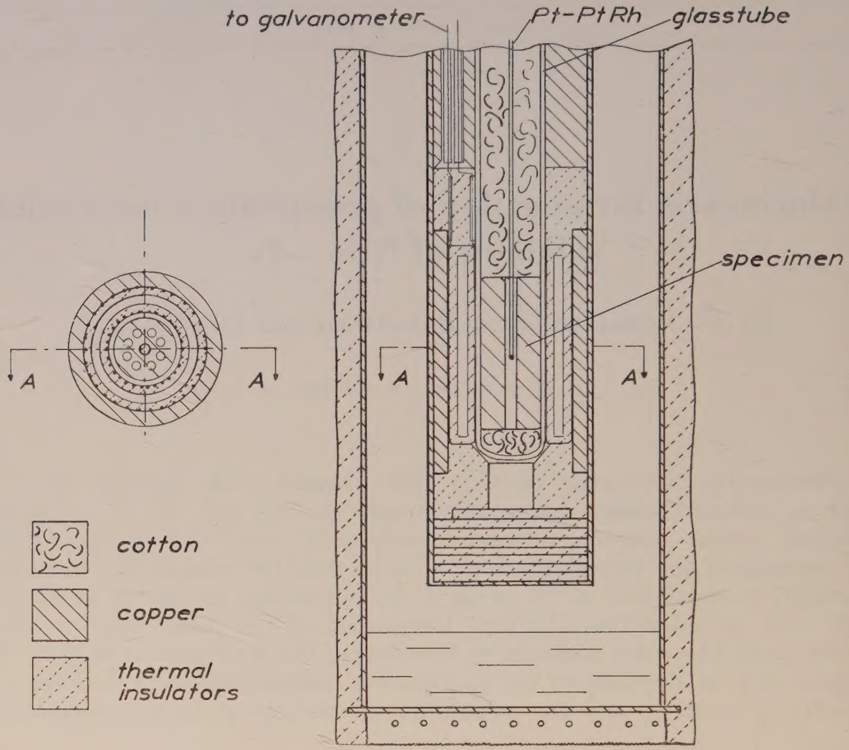

Fig. 1. Experimental arrangements.

the temperature variations very small. Thus the current heating the boiling water was taken from a voltage-regulated generator. The water for the cooling of the return-flow condenser, which had to be taken from the water mains, was kept at as constant a temperature as possible by strong and continuous flow. The thermostat was thermally well insulated. The ballast vessel, which contained nitrogen of suitable pressure and had a volume of about 0.15 m^3, was placed in a thermally insulated tank containing about 1 m^3 of water, continuously stirred and protected against evaporisation by a layer of oil. The temperature of this water was measured to 0.001° C by means of a Beckman thermometer, and the variations were, if necessary, accounted for by an empirically determined correction of the readings. The whole arrangement was placed in a room without windows or external walls which was kept at a constant temperature within ± 0.2° C by means of an air-conditioning installation. The room had also good foundations for the galvanometer and the tube and scale. From the thermocouples of the apparatus, thermally well insulated copper wires led to a likewise well insulated commutator of copper and from there to the galvanometer.

3. The specimens and their heat treatment. The specimens were prepared from a bar of pure technical iron, kindly placed at our disposal by Bergsingenjör TORKEL BERGLUND at the Sandvikens Jernverks A.B. According to the chemical analysis it contained in weight percent: 0.017 C, 0.01 Si, 0.07 Mn, 0.002 P and 0.007 S. The content of N was not determined, but we know from our own investigations that it was probably less than 0.003 %. The specimens were first decarburized in wet hydrogen gas at 720 °C for about two days. During this time the loss in weight reached a constant, final value which corresponded well to the carbon content as stated. The specimens were then nitrated according to methods described by PARANJPE (1) in a mixture of H_2 with 25 mol% NH_3 at 580 °C during 5 to 10 hours. The amount of nitrogen absorbed was determined from the increase in weight. The two specimens used for our measurements contained: nr 9 0.07, and nr 10 0.11 weight% of N. In nr 9 the solution of N in α-Fe could be expected to remain saturated in equilibrium with Fe_4N up to about 500 °C, and in nr 10 up to the eutectoid point at 590 °C. The specimens were homogenized for 24 hours at 580° in a protecting gas mixture of N_2 and 5 % H_2.

Before each measurement the specimen was heated for one hour at 580 °C and slowly cooled down to the temperature of the test, where it was kept for 16 hours in order to obtain full equilibrium. From here it was quenched in ice-cooled water and then rapidly, in two or three minutes, heated in an oven, the temperature of which was about 300 °C, up to the temperature of the measuring apparatus, the temperature of the specimen being controlled by means of the thermocouple placed in its central hole. The moment the specimen passed the temperature of the measuring apparatus (70 or 94 °C) it had to be carried quickly to this apparatus and the readings on the galvanometer had to start.

4. Measurements and results. During the measurements the galvanometer was usually read, and the current commutated, once a minute. When the evolution of heat was small, a mean value had to be taken over one or several hours. Figure 2 shows two examples of curves obtained.

The beginnings of the curves are always somewhat irregular because of the impossibility of making the initial temperature of the specimen exactly that of the thermostat. It seems most probable, however, that the evolution of heat starts from zero. To permit integration we have extended the curves linearly to the zero point, though in fact our measurements so far give no certain information about the kinetics in the starting point. We intend to investigate the kinetics more in detail later.

The shape of the curves is uncomplicated with a simple maximum and thereupon a continuous decrease to zero. The zero line does not mean zero deflection of the galvanometer as there are always some constant thermo-electric forces in the circuit. The zero line was determined at the end of each measuring series. After the end of each series the apparatus was also calibrated by Peltier heat. If the heating power P is constant we have $P = a \cdot s$, where s is the net deflection of the galvanometer and a constant. If P varies strongly with the time t the thermal inertia of the specimen and apparatus causes a certain correction, and we have

$$P = a s + b \frac{d s}{d t} \tag{1}$$

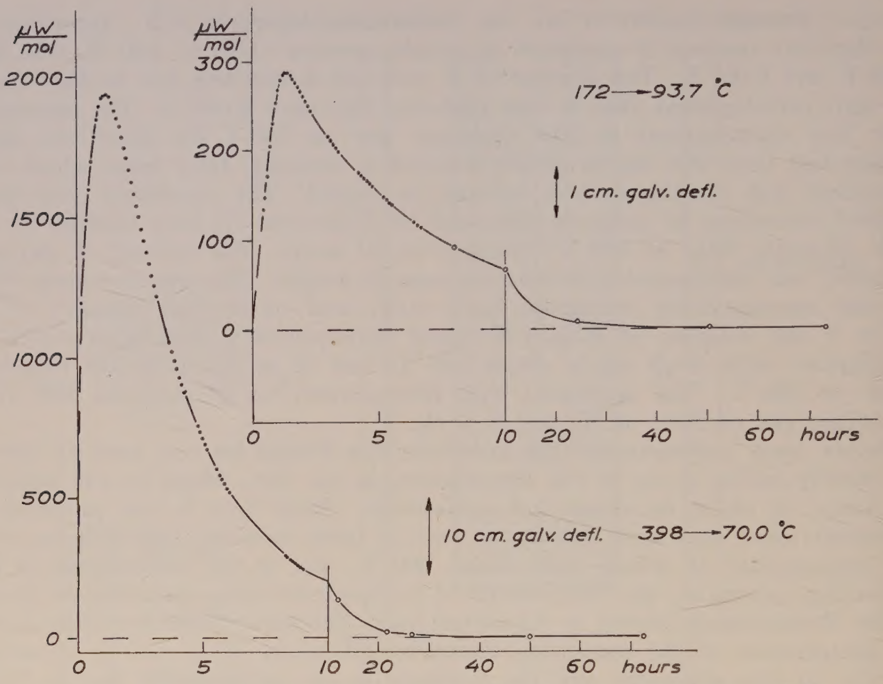

Fig. 2. Experimental power-time curves. Power in microwatt per mol Fe.

where b is another constant. Both constants a and b might be obtained from the calibration. As we are here mainly interested in the total heat evolved, which is simply

$$Q = \int_0^\infty P\,d\,t = a\int_0^\infty s\,d\,t, \qquad (2)$$

the integral of the second term in (1) being zero, since s is zero at both limits, we have not added the correction term to the curves which thus give the product $a \cdot s$. The values of Q obtained by integration are collected in Table 1 under "Q observed".

Table 1

Specimen nr	Measuring temp. °C	Equilibrium temp. °C	Q observed Joule/mol	Q corrected Joule/mol	$\frac{Q}{L}$ $z = \mathrm{N/Fe}$	Weight % N
9	93.5	172	3.85	5.3	0.00024	0.006
»	93.7	187	5.5	6.9	0.00031	0.008
»	93.8	208	5.9	7.3	0.00033	0.008
»	93.5	241	10.9	12.3	0.00055	0.014
»	93.9	288	14.5	15.9	0.00072	0.018
»	70.0	330	22.5	23.3	0.00105	0.026
»	69.9	398	37.0	37.9	0.00170	0.043
10	69.8	451	51.8	52.6	0.00236	0.059
»	69.9	575	85.0	85.8	0.00385	0.097

5. Calculation of latent heat and solubility. For a calculation, from our results, of the heat of solubility L per mol of Fe_4N in α-Fe we must first discuss the temperature dependence of this quantity. The energy principle gives for the difference in L at two temperatures T_1 and T_2

$$L_2 - L_1 = \int_{T_1}^{T_2} (4\,C_{\mathrm{Fe}} + C_{\mathrm{N}} - C_{\mathrm{Fe_4N}})\,dt \tag{3}$$

where C_{Fe} is the heat capacity per mol for α-Fe, C_{N} the same for N in dilute solution in α-Fe, and $C_{\mathrm{Fe_4N}}$ the same for the nitride. If each atom had the normal heat capacity of solids, about 25 Joule (or 6 calories) per gram atom and degree, the difference should be zero. However, the heat capacities of ferromagnetic substances are known to be anomal with a peak at the Curie point. For α-Fe the Curie point is at 768 °C, and thus outside the range of temperature that is of interest in our case, but the anomalies are already appreciable within this range, C increasing from the value 27 at 70 °C to 41 at 575 °C. For Fe_4N the Curie point is at 485 °C but we have found no measurements of C in the literature covering the range considered. The heat capacity of N dissolved in α-Fe is unknown and scarcely determinable. Thus we do not even know the sign of the sum within the brackets of equation (3). It is well possible that it changes sign once or twice in our range of temperature. The simplest thing to do in this situation is to calculate approximately assuming a constant mean value of L for the range.

As the solubility of N in α-Fe is small, we may approximately write the atomic ratio z of N to Fe in the saturated solution as

$$z = A\,e^{-\frac{L}{RT}} \text{ or } \ln z = \ln A - \frac{L}{R} \cdot \frac{1}{T} \tag{4}$$

where A is an unknown constant and R the gas constant. If the solubility at the temperatures of the calorimetric measurements is negligible the heat evolved is

$$Q = L\,z \tag{5}$$

where z is the initial concentration after quenching. Eqs. (4) and (5) give

$$\ln Q = \ln L + \ln A - \frac{L}{R} \cdot \frac{1}{T} \tag{6}$$

and $\ln Q$ plotted against $1/T$ give a straight line from the slope of which L is obtained. In our case, however, the solubility z_0 at the measuring temperatures is small but not negligible. We therefore have

$$Q = Q_{\mathrm{obs}} + L\,z_0 \tag{7}$$

where Q_{obs} are the observed values given in Table 1. We thus have had to calculate Q by successive approximations, using a $\log Q - 1/T$-diagram, and starting with the approximation $L\,z_0 = 0$. These calculations have given the corrected values of Q in Table 1, and the empiric values

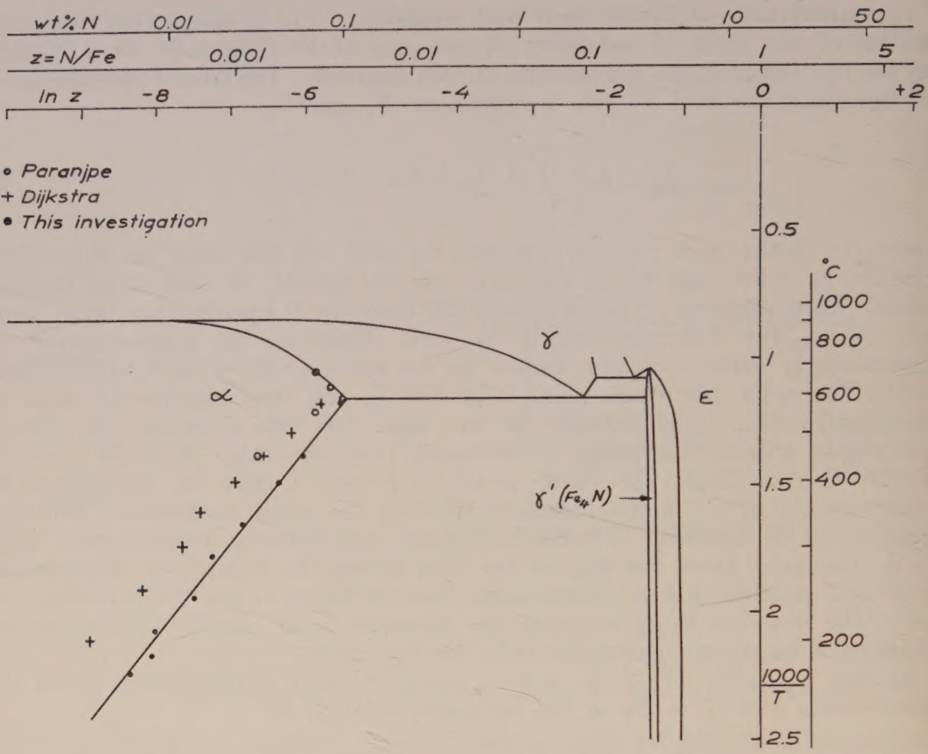

Fig. 3. Part of the logarithmic equilibrium diagram Fe-N.

$$L = 22\,300 \text{ Joule/mol} \tag{8}$$

and

$$A = 0.093. \tag{9}$$

The solubilities z which according to (5) are proportional to the Q and given by $z = Q/L$, are collected in the last column of the Table. In Fig. 3 we have plotted as filled circles the logarithms of z against $1/T$. In accordance with Eq. (4) they lie within reasonable limits on a straight line.

6. Discussion of results. A diagram of the type of Fig. 3 is, as has been pointed out earlier by one of the authors (2), a very suitable type of equilibrium diagram when small solubilities have to be considered. We have in this diagram also included some of the other boundary lines of the system Fe-N according to data determined or selected by Paranjpe and collaborators (1). Concerning the maximum solubility at the eutectoid temperature 590 °C, our results agree well with those of Paranjpe obtained by a nitrogenizing method. Both investigations give a maximum solubility of 0.10 % by weight.

The only earlier extensive investigation covering the same range of temperature as our measurements is a recent investigation of Dijkstra (3) made by means of the damping method. From his partly rather complicated results, Dijkstra concludes that two different precipitates exist, an intermediate phase and the final stable phase Fe_4N. The concentration of nitrogen in solution in the α-iron is found to be appreciably higher in equilibrium with the intermediate phase than with the Fe_4N-phase. Our solubility values for low temperatures agree well with those values of DIJKSTRA which are connected with the intermediate phase, whereas with respect to the tempering times used in our investigation and according to the results of DIJKSTRA, we should have expected the final equilibrium with Fe_4N to be well established. The results of DIJKSTRA, which he has indicated as those best representing the equilibrium with Fe_4N, are included in Fig. 3 as crosses. At low temperatures these solubilities are only about half of those calculated from our results. The cause of this discrepancy is not evident. A weak point in our case might be the calculation of the solubulities by means of Eq. (4) with constant values for A and L. A weak point in the determinations of DIJKSTRA might be the way in which the absolute values are obtained. The internal friction measurements have directly only given relative values for varying temperatures, which do not deviate too much from our relative values. The absolute values were obtained indirectly and probably with less accuracy from resistivity measurements. But there are also other possibilities for discrepancies in the differences between the two investigations in respect to the heat treatments, the dimensions of the specimens, and the atmospheres in which they were kept. It seems impossible to settle the origin of the discrepancies without further experimental study.

According to theory, the constant A of Eq. (4) gives the number of possible sites in the α-Fe lattice for a dissolved N-atom in proportion to the number of Fe-atoms. It is remarkable that our experimental value $A = 0.09$ is so much smaller than unity. A similar result has been obtained by WERT (4) for C in α-Fe.

The present investigation has been supported by a grant from the Swedish Council for Technical Research. It has been made partly in parallel with a similar calorimetric investigation of the precipitation of carbon dissolved in α-iron, which, however, being more difficult because of the smaller solubility of carbon than of nitrogen, has not yet given final results.

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LITERATURE. (1) **V. G. Paranjpe**, Thesis M I T 1949. **V. G. Paranjpe, Morris Cohen, M. B. Bever** and **C. F. Floe**, Journal of Metals **188** (1950) 261. — (2) **G. Borelius**, Ann. d. Physik **28** (1937) 507. — (3) **L. J. Dijkstra**, Journal of Metals **1** (1949) 252. — (4) **C. A. Wert**, Journal of Metals **188** (1950) 1242.

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